MASS PRODUCTION, SELECTIVE FORMATION, AND APPLICATIONS OF CARBON NANOTUBES

Morinobu Endo

Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano-shi 380-8553, Japan

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Abstract

Extra-ordinary chemical and physical properties of carbon nanotubes [1, 6] and also the success of large-scale production by a catalytic chemical vapor deposition method, particularly with the use of a floating reactant technique [2-4], make them applicable in the fabrication of adsorbent, electrochemical electrode, field emitter and functional filler in composite at a possible low cost. Through judicious selection of transient metal, support materials and synthetic conditions (temperature, duration), it is possible to produce different types of carbon nanotubes such as multi-walled carbon nanotubes (MWNTs), double-walled carbon nanotubes (DWNTs) and single-walled carbon nanotubes (SWNTs) selectively. In this study, we will describe the catalytic synthesis of various carbon nanotubes from the point of synthetic conditions, and structural changes by heat treatment will be discussed in terms of structural stability, and finally their practical applications of these carbon nanotubes will be described from the industrial point of view.

It is possible to obtain various fibrous carbons which exhibit a wide range of diameters from 200 to 1 nm, different crystallinity and different angle of graphene sheet with regard to tube axis through exact control of synthetic conditions of catalytic chemical vapor deposition (CCVD) method. Recently, the development of the floating reactant technique made possible to the large-scale production of carbon nanofibers (CNFs) and MWNTs [4]. In the synthesis of SWNTs, nano-sized SiO_2 impregnated with Fe-containing compounds (seeding method) were fed into the reactor (around 1000^{o}C) with benzene as carbon feedstock, and with hydrogen as the carrier gas [7]. In contrast to current CVD methods, this combinational technique allows high yield efficiency of the nanotubes. A detailed TEM and Raman studies revealed that there are large variations in textures (isolated and bundle) and also diameters (see Fig. 1 (a)).

The recent hot topic is the synthesis of DWNTs because these tubes are more thermally and chemically stable when compared to SWNTs; they also exhibiting the 1D character of a quantum wire. In addition, DWNTs could also be used in the fabrication of electron field emitter and nano-composites. The synthesis of DWNTs was carried out using a conditioning catalyst (Mo/Al_2O_3) on one end of the furnace, and the nanotube catalyst (Fe/MgO) in the middle part of the furnace (see supplemental information). Subsequently, a CH_4+Ar gas mixture (1:1) was fed into the reactor for 10 minutes at 875°C. When using the conditioning catalyst, preferential growth of DWNTs over SWNTs occurred, possibly due to an increased portion of active carbon species. In order to obtain a pure DWNT, a two-step purification process was applied to the synthesized products. In particular, HCl treatments were carried out in order to remove iron catalyst and the supporting material, followed by air oxidation at 500^{o}C for 30 minutes. The latter process is used to remove amorphous carbon and chemically active SWNTs. After a filtering process, we obtained a dark and stable paper-like sheet, which is very flexible and mechanically stable (tough). Careful HRTEM (JEOL JEM-2010FEF) observations revealed an extremely high-yield of DWNTs (more than 95%) arranged in bundles. Fig. 1 (b) exhibit cross sectional image of HR-TEM images of DWNTs bundles. When heat treated at higher temperature in inert atmospheres, unusual phenomena occur in DWNTs bundles. HRTEM image of Figure 1 (c) exhibits a sequential reconstruction behaviors of DWNTs at 2100^{o}C [9]. Two adjacent outer shells start to merge (see, (I) in Fig. 1 (c)) via a zipping process, similar to the coalescence of SWNTs under electron beam irradiation, and a large single outer shell with an oval shape is formed (see, (II) in Fig. 1(c)). The process occurs due to the coalescence and reconstruction of the outer shells of DWNTs, leaving the inner cylinders almost intact, the latter being encapsulated inside the large diameter coalesced tubule (bi-cable). We envisage this material to be useful in the fabrication of novel sensors, nanocomposites, field emission sources, nanotube bi-cables and electronic devices. On top of that, it is expected that DWNTs will replace SWNTs or MWNTs for various specific applications due to their expected superior mechanical properties, thermal conductivity and structural stability derived from their unique coaxial structure.

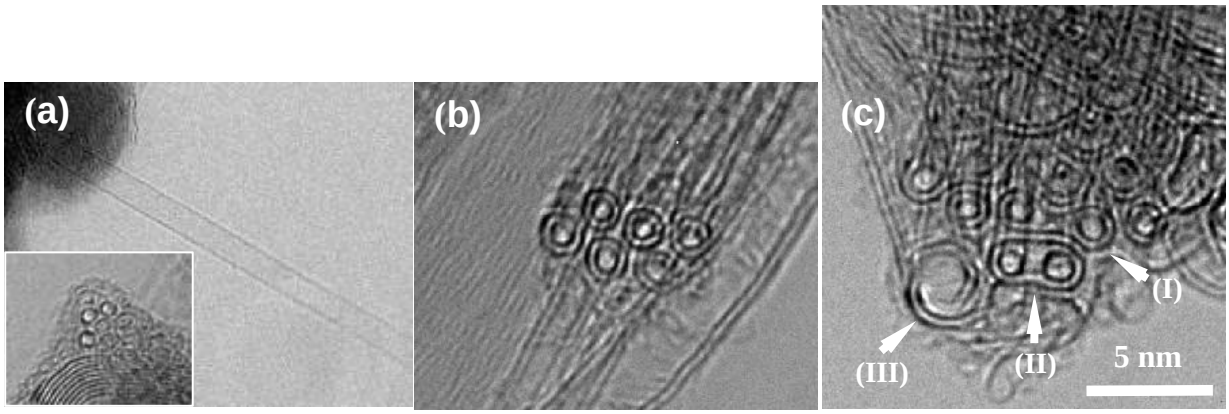

Figure 1. (a) typical HRTEM image of single wall carbon nanotubes, (b) Typical high resolution transmission electron microscopy (HRTEM) image of DWNTs in a bundle state, (c) HRTEM image of DWNTs at 2100°C. This image exhibits a sequential reconstruction process of a DWNT: (I) two outer tubes start to merge, through a zipping mechanism, (II) two outer tubes are completely combined into a single large outer tube with an oval shape containing two SWNTs, and (III) two inner SWNTs in a confined space might decompose along the inner wall of an outer shell, to form one inner single shell, like the formation of a DWNT derived from a peapod

REFERENCES

1. Dresselhaus, M. S., et al., *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego (1996).
2. Oberlin, A.; Endo, M.; Koyama, T.: “Filamentous Growth of Carbon through Benzene Decomposition," J. Cryst. Growth 32, 335 (1976).
3. Endo, M. et al., “The production and structure of pyrolytic carbon nanotubes (PCNTs),” J. Phys. Chem. Solids 54, 1841 (1993).
4. Endo, M. “Grow Carbon Fibers in the Vapor Phase,” Chem. Tech. (Leipzig) 18, 568 (1988).
5. Endo, M. et al., “Vapor-grown carbon fibers (VGCFs) Basic properties and battery application,” Carbon 39, 1287 (2001).
6. Iijima, S. “Helical microtubules of graphitic carbon,” Nature, 354, 56 (1991).
7. Hayashi, T. et al., “The smallest freestanding single-wall carbon nanotube,” Nanoletters 3, 887 (2003).
8. Endo, M. et al., “Buckypaper from coaxial nanotubes,” Nature 433, 476 (2005).
9. Endo, M. et al, “Coalescence of Double-walled Carbon Nanotubes: Formation of Novel Carbon Bi-cables,” Nano letters 4, 1451 (2004).